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ABSTRACT

This booklet, one of a series of 17 developed at Prince George's Community College, Largo, Maryland, provides an individualized, self-paced undergraduate organic chemistry instruction module designed to augment any course in organic chemistry but particularly those taught using the text "Organic Chemistry" by Morrison and Boyd. The entire series of modules covers the first 13 chapters of the Morrison-Boyd text in great detail. Each module has been provided with from one to three audiotapes, available from Prince George's Community College, to provide students additional explanations of particular concepts. Each module includes a self-evaluation exercise, a reference guide, worksheets to be completed with the audiotapes, answer sheets for the worksheets, a progress evaluation, an answer sheet for the progress evaluation, an answer sheet for the self-evaluation exercise, an introduction to the topic covered by the module, and student performance objectives for the module. The topic of this module is alicyclic compounds. (SL)

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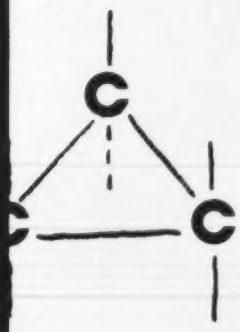
ORGANIC CHEMISTRY



V. Zdravkovich

14

S elf
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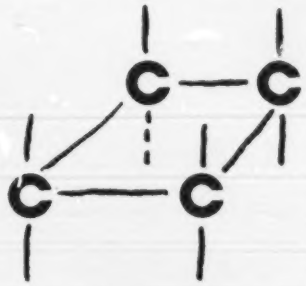

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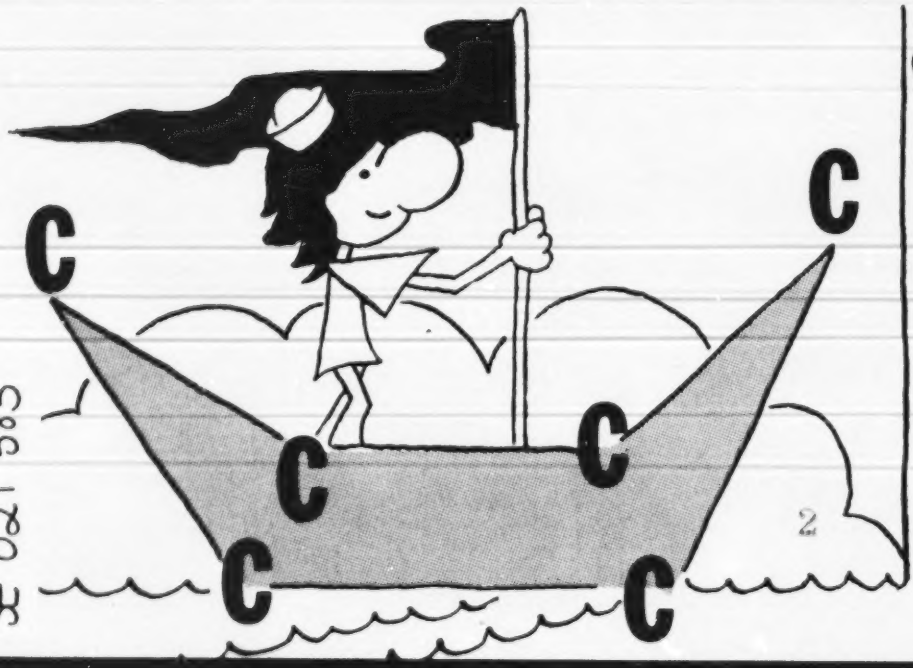
CYCLIC COMPOUNDS



Self Instructional Sequence in

ORGANIC CHEMISTRY

"Copr.," V. Zdravkovich 1976

Self Instructional Package No. 14

ALICYCLIC COMPOUNDS

Introduction

In this Self Instructional Package you will learn about the structural theory as applied to ring compounds. It was stated for the first time by a man who started experimenting with plants when he was eight years old, made his first chemical discovery when he was twelve, published three hundred scientific or more precisely chemical articles and lifted himself to the heights of international fame. His name is Adolph von Baeyer. In the course of his work he often made mistakes but his love for truth and the advancement of science allowed him to admit them publicly. As he himself put it, "why should one obstinately retain a certain opinion?" One of his errors is discussed in this self instructional package.

In addition to learning about his theory and marveling at the lucidity of a mind which could conceive such ideas, understanding the error he made, you would perhaps like to explore Baeyer's personality. His own words can best help you to do that.

"What characterizes a great scientist? He should not issue orders, but listen, and adapt and remake himself according to what he has heard....This was the method of the ancient empiricists: they put their ears to nature. The modern scientist does the same thing, and I have tried to do likewise. It has a very peculiar effect on men when they get close to nature. They then develop quite differently as compared with those who approach nature with a preconceived idea. Everyone who comes to nature with his mind made up will, to an extent, stand before nature like a general. He will have a desire to order her around....I have never planned my experiments to find out if I were right, but to see how the compounds behave. This is the reason also why I am so indifferent to theories."

Self Instructional Package No. 14
Form A - List of Objectives

ALICYCLIC COMPOUNDS

Definitions

The student will be able to define and illustrate with appropriate examples, where applicable, the following terms: CARBOCYCLIC compounds, ALICYCLIC compound, CYCLIZATION reaction, SINGLET METHLENE, TRIPLET METHYLENE, CARBENE, ANGLE STRAIN, TORSIONAL STRAIN, Baeyer theory, CHAIR CYCLOHEXANE, BOAT CYCLOHEXANE, TWIST CYCLOHEXANE, AXIAL POSITION, EQUATORIAL POSITION, CYCLOADDITION reaction.

Preparations

The student will be able to write the reactions for the preparation of alicyclic compounds from its derivatives.

The student will be able to write the reactions for the preparation of cyclopropane and cyclobutane from open chair compounds.

The student will be able to write the reactions for the addition of methlene and substituted carbenes to an alkene.

Reactions

The student will be able to identify the products in the reaction of cyclopropane and cyclobutane with halogens, hydrogen, hydrogen iodide, sulfuric acid and potassium permanganate.

The student will be able to complete the reactions of cycloalkanes, cycloalkenes, cyclodienes and cycloalkynes with a variety of reagents.

Multi-step Synthetic Schemes

The student will be able to devise multi-step synthesis schemes for the synthesis of different alkanes from a given reactant.

The student will be able to identify all the reagents in a given multi-step synthetic scheme.

The student will be able to identify the intermediate compounds formed in a multi-step synthetic scheme.

Isomerism

The student will be able to identify all the structural isomers for a given derivative of an alicyclic compound.

The student will be able to identify all the possible stereoisomers of different disubstituted derivatives of cyclic compounds.

The student will be able to identify given isomers as: structural or stereoisomers; enantiomers or diastereoisomers; configurational or conformational isomers; optically active or inactive stereoisomers.

Self Instructional Package No. 14
Form B - Self Evaluation Exercise

ALICYCLIC COMPOUNDS

Identify the statements below as true or false by placing a capital T or F in the spaces provided on the left.

1. _____ The larger the deviation from the tetrahedral angle, greater the stability of the compound.

2. _____ Cycloaddition reactions of cyclopropane illustrate its low stability.

3. _____ The puckered shape of cyclohexane is the reason for its stability.

4. _____ A tetrahedral bond angle provides maximum overlap of the SP^3 atomic orbitals.

5. _____ Cyclopentane yields pentane when heated with hydrogen in presence of a catalyst.

6. _____ Cyclopropane yields propane when heated with hydrogen in presence of a catalyst.

7. _____ In the reaction of cyclopropane with bromine in presence of $FeBr_3$ bromo cyclopropane is produced.

8. _____ The major product in the reaction of 1-methyl cyclopropene with HBr is 1-bromo-2-methyl cyclopropane.

9. _____ Chair conformation of cyclohexane is more stable than the boat conformation.

10. _____ Baeyer theory with regard to cyclohexane is widely used today.

11. _____ Greater the overlap of atomic orbitals stronger the bond.

12. _____ Addition of methylene to a cis alkene in the gaseous phase yields cis cyclopropane derivative.

13. _____ Presence of oxygen in the reaction of an alkene with diazomethane in presence of light causes syn addition or stereospecific reaction.

SIP No. 14
Form B - Self Evaluation Exercise

Blacken out the correct answer or answers in the questions below.

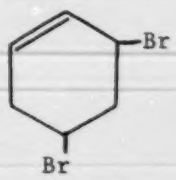
14. Experimentally observed heat of combusion per CH_2 group in compound A is 157.4 kcal/mole In compound B the heat of combustion per CH_2 group is 162.5 kcal/mole. These facts lead to the following conclusions:

a) Compound A is more stable than compound B.

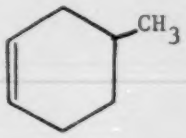
b) the overlap of the atomic orbitals in compound A is more complete.

c) The internuclear angles in compound A deviate significantly from the tetrahedral angle.

d) Compound B is more stable than compound A.

15. The correct IUPAC name for the  is:

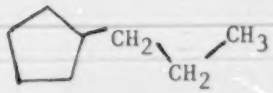
a) 2,4-dibromo cyclohexene
b) 3,5-dibromo cyclohexene
c) 4,6-dibromo cyclohexene
d) 1,3-dibromo-4-cyclohexene

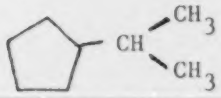
16. The correct IUPAC name for  is:

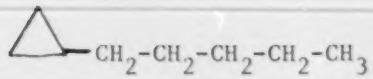
a) 4-methyl cyclohexene
b) 1-methyl-3-cyclohexene
c) 5-methyl-cyclohexene
d) 3-methyl-1-cyclohexene

17. The correct structure corresponding to cyclopropyl cyclopentane is:

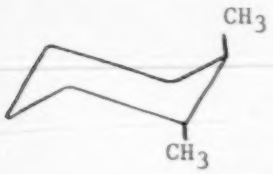
a)

b) 

c) 

d) 

18. The correct statements about the compounds below are:

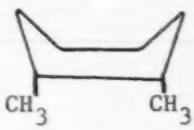


Relative to each other -

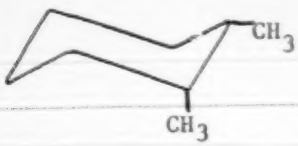
a) Relative to each other they are conformational isomers
b) they are both cis stereoisomers
c) they are both optically active
d) they are both trans stereoisomers

19. The correct statements about the compounds below are:

a) they are diastereoisomers relative to each other
b) they are both cis stereoisomers
c) they are both optically active when separated
d) they are configurational isomers.

20. Relative to each other compounds 

and



are:

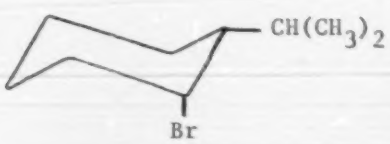
a) diastereoisomers
b) conformational isomers
c) enantiomers
d) configurational isomers

21. When 2.4-dichloro pentane is heated with zinc the major product is:

a) 2,4-pentadiene
b) cyclopropane
c) 1,2-dimethyl cyclopropane
d) 2-pentyne

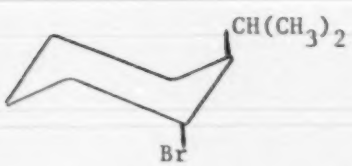
22. The major product in the reaction of 1-isopropyl cyclohexene with HBr is:

a)

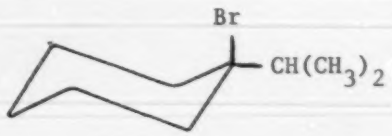


c)

b)



d)



23. When cis-2-hexene reacts with chloroform in presence of potassium tertiary butoxide, the major product is:

a) cis-1-methyl-2-propyl cyclopropane
b) trans-1-methyl-2-propyl cyclopropane
c) racemic mixture of trans-1-methyl-2-propyl cyclopropane
d) mixture of cis and trans-1-methyl-2-propyl cyclopropane

24. The reaction of cyclopentene with aqueous solution of $KMnO_4$ will produce as a major product:

a) trans 1,2-cyclopentane diol
b) cis 1.2-cyclopentane diol
c) racemic mixture of the trans 1,2-cyclopentane diol
d) mixture of cis and trans 1.2-cyclopentane diol

25. The correct statements about the 1,3-dimethyl cyclohexane and 1,4-dimethyl cyclohexane are:

    a) cis-1,3-dimethyl cyclohexane exists as a diaxial and di-equatorial conformation

    b) trans-1-4-dimethyl cyclohexane exists in two enantiomeric forms

    c) cis-1,4-dimethyl cyclohexane exists in two enantiomeric forms

    d) trans-1,3-dimethyl cyclohexane exists in two enantiomeric forms

Self Instructional Package No. 14
Form C - Reference Guide

ALICYCLIC COMPOUNDS

The Reference Guide should be used in conjunction with Form B or the Self Evaluation Exercise. The references give the correlation between the questions in Form B and the available material in the textbook and in the form of tapes.

Questions 1, 4, 11	Chapter 9, Sections 7, 9	Morrison & Boyd
Questions 2, 5, 6, 7	Chapter 9, Section 6	Organic Chemistry
Questions 3, 10, 14	Chapter 9, Sections 8, 9	
Question 8	Chapter 9, Section 5	
Question 9	Chapter 9, Section 11	
Questions 12, 13	Chapter 9, Section 15	
Questions 15, 16, 17	Chapter 9, Sections 1, 2	
Questions 18, 19, 20, 25	Chapter 9, Sections 13, 14	
Question 22	Chapter 9, Sections 5, 12	
Question 23	Chapter 9, Section 16	
Question 24	Chapter 9, Sections 13, 14; SIP No.	
Question 21	Chapter 9, Section 4	

For Questions 1, 2, 4, 5, 6, 7, 8, 11, 12, 13, 14, 21, 23, 24

additional explanations and examples can be found in Tape 1 - Alicyclic Compounds - Small ring compounds.

For Questions 3, 9, 10, 18, 19, 20, 22, 25

additional explanation and examples are provided in Tape 2 - Alicyclic Compounds - Cyclohexane

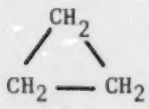
Learning without thought
is labor lost; thought
without learning is perilous.
Confucius (6th. B.C.)

Self Instructional Package No. 14
Tape 1 - Work Sheet

ALICYCLIC COMPOUNDS

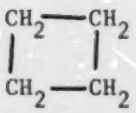
SMALL RING COMPOUNDS

Example No. 1



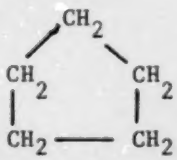
OR

cyclopropane



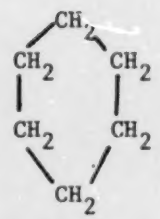
OR

cyclobutane



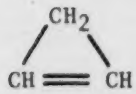
OR

cyclopentane



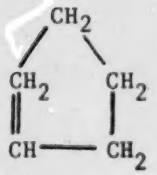
OR

cyclohexane



OR

cyclopropene



OR

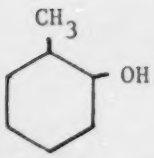
cyclopentene

SIP No. 14
Tape 1 - Work Sheet

Example No. 2

The correct name is:

a) 1-methyl-2-cyclopentene
b) 3-methyl cyclopentene
c) 5-methyl cyclopentene
d) 1-methyl-4-cyclopentene



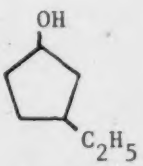
The correct name is:

Assignment No. 1

Assign the correct IUPAC names to the following compounds:

a)

b)



c)

d)

Assignment No. 2

Draw the structures that correspond to the following compounds:

a) 3-isopropyl cyclopentene

SIP No. 14
Tape 1 - Work Sheet

Assignment No. 2 (continued)

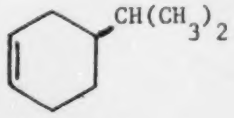
b) 2,4-dimethyl-1,3-cyclohexadiene

c) 4-methyl-cyclopentene-2-ol

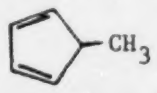
d) 3,3,5-trimethyl cyclopentene

Assignment No. 3

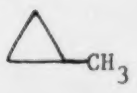
Saturated Sam was asked to assign the correct IUPAC names to a number of compounds. His answers are given below. Examine them carefully and rectify his state of confusion.

a) 

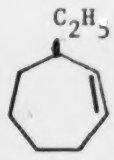
3-propyl-cyclohexene

b) 

1-methyl-2,4-cyclopentadiene

b) 

methyl cyclopropane



3-ethyl-1-cyclohexene

SIP No. 14
Tape 1 - Work Sheet

Example No. 3 - Preparation of cyclic compounds

1. From an open chain compound - CYCLIZATION
2. From the cyclic derivative

CYCLIZATION:

$BrCH_2-CH_2-CH_2Br \xrightarrow{Zn,\ heat}$

$BrCH_2-CH_2-CH_2-CH_2Br \xrightarrow{Zn,\ heat}$

$\xrightarrow{H_2, Pd \text{ or } Pt}$ (hydrogenation of the double bond)

$\xrightarrow{?}$ (dehydration of the alcohol)

Assignment No. 4

Identify the reagents required for the preparation of the following compounds from the reagents listed on the left

bromocycloheptane ⟶ cycloheptene

1,2-dibromocyclopentane ⟶ cyclopentene

1,2-dibromocyclohexane ⟶ cyclohexyne

cyclopropene ⟶ cyclopropane

SIP No. 14
Tape 1 - Work Sheet

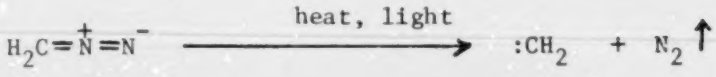
Assignment No. 5

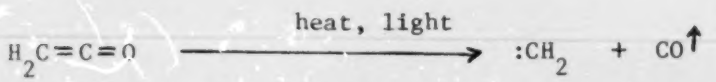
Identify all the steps in the multi-step laboratory synthesis of:

1,3-cycloheptadiene	from	cycloheptane
cyclopentane	from	cyclopentanol
1,2-cyclohexanediol	from	cyclohexane

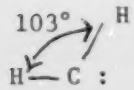
SIP No. 14
Tape 1 - Work Sheet

Example No. 5 - preparation of methylene

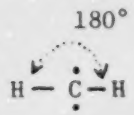




methylene or carbene

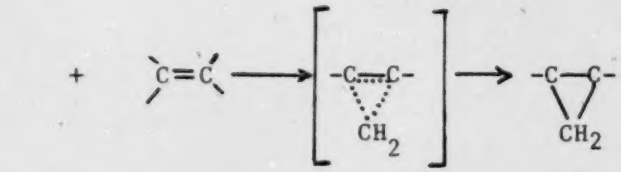


SINGLET methylene - unshared electrons are paired



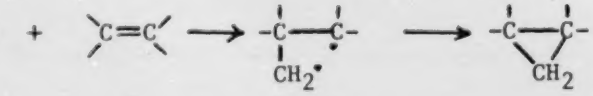
TRIPLET methylene - unshared electrons are not paired - a diradical

Example No. 6 - mechanism of the cycloaddition reaction



stereospecific-syn addition

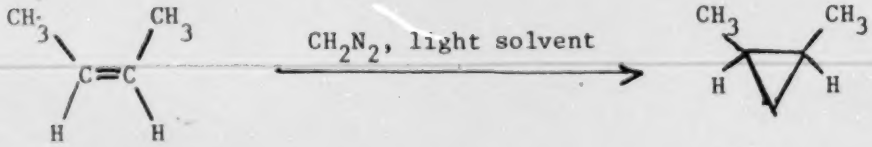
singlet methylene transition state



non-stereospecific addition

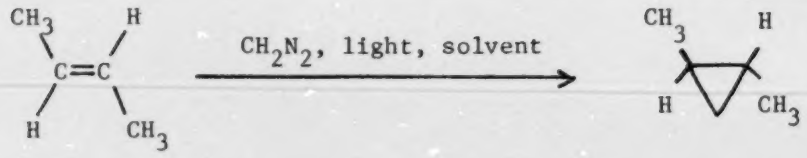
triplet methylene

Example No. 7



cis-2-butene

Example No. 7 (continued)



trans-2-butene

Assignment No. 6

Identify the products in the following reactions:

cis-3-hexene $\xrightarrow{CH_2N_2,\ light}$

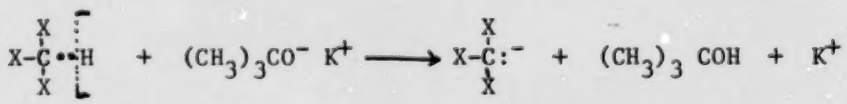
trans-3-hexene $\xrightarrow{CH_2N_2,\ light,\ O_2}$

cis-2-hexene $\xrightarrow{CH_2CO,\ light}$

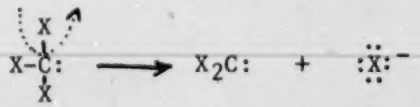
trans-2-hexene $\xrightarrow{CH_2N_2,\ light,\ liquid\ phase}$

Example No. 8

Step 1 - Abstraction of the hydrogen positive ion by the base -



Step 2 - Repulsion of the halide anion -

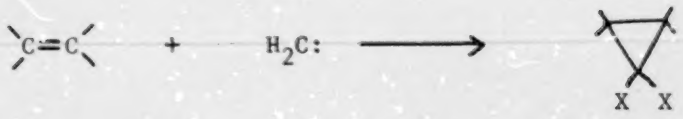


dihalo carbene (neutral)

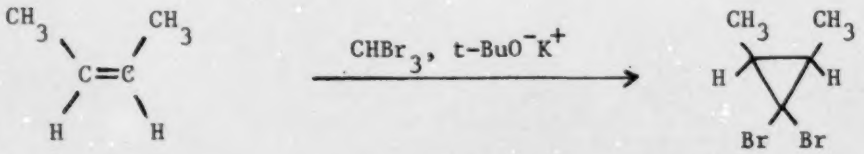
SIP No. 14
Tape 1 - Work Sheet

Example No. 8 (continued)

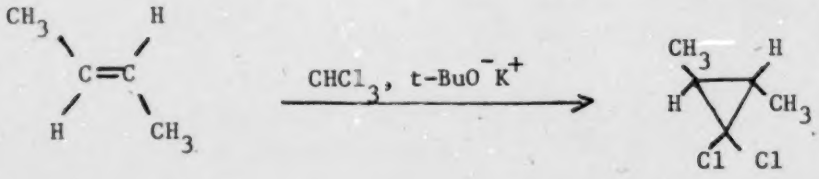
Step 3 - cycloaddition



Example No. 9 - Stereospecific addition of dinalocarbene

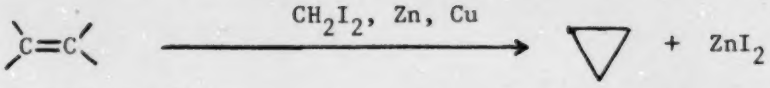


cis-2-butene



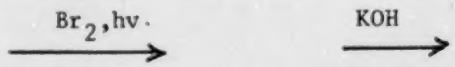
trans-2-butene

Example No. 10



Assignment No. 7

Draw the structure and name the products in the following reactions:

a) cyclopentane 

SIP No. 14
Tape 1 - Work Sheet

b) 1,3-cyclohexadiene $\xrightarrow{Br_2,\ CCl_4}$

c) cycloheptene $\xrightarrow{KM_nO_4,\ ag}$

d) cyclopentene $\xrightarrow{\text{hot } KM_2O_4}$

e) cycloheptyne $\xrightarrow{\text{excess HBr}}$

f) 1-methyl cyclopentene $\xrightarrow{HBr,\ \text{peroxide, light}}$

g) cyclohexene $\xrightarrow{Br_2,NBS,\ \text{light}}$

h) 1-methyl cyclohexene $\xrightarrow{HBr}$

i) 1,3-cyclopentadiene $\xrightarrow{H_2O,\ H^+}$ $\xrightarrow{H_2,Pt}$

Assignment No. 8

Identify (draw the structures and name) the reactants in the following reactions:

a) $\xrightarrow{\text{acid}}$ 3-methyl cyclopentene

SIP No. 14
Tape 1 - Work Sheet

Assignment No. 8 (continued)

b) $\xrightarrow{HBr}$ 1-bromo-1-ethyl cyclohexane

c) $\xrightarrow{Br_2, CCl_4}$ 3,5-dibromo cyclopentene + 3,4-dibromo cyclopentene

d) $\xrightarrow{CHBr_3,\ t\text{-}BuO^-K^+}$ 1,1-dibromo-2,3-dimethyl cyclopropane

e) $\xrightarrow{CH_2N_2,\ light\ O_2}$

f) $\xrightarrow{HBr}$ 1,1-dibromocyclobutane

g) $\xrightarrow{O_3, H_2O, Zn}$ $HOOC\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COOH$

Example No. 11 - Reactions of

		Expected product	Observed product	Reaction
	$\xrightarrow{KM_nO_4}$	N.R.	$HOCH_2CH_2CH_2OH$	addition
	$\xrightarrow{KM_nO_4}$	N.R.	N.R.	N.R.

Example No. 11 (continued)

	Expected product	Observed product	Reaction
KM_nO_4	N.R.	N.R.	N.R.
conc H_2SO_4	N.R.	$CH_3CH_2CH_2OH$	addition
conc H_2SO_4	N.R.	N.R.	N.R.
conc H_2SO_4	N.R.	N.R.	N.R.
X_2, Fe	N.R.	$X\text{-}CH_2CH_2CH_2\text{-}X$	addition
X_2, Fe	N.R.	N.R.	N.R.
X_2, Fe	N.R.	N.R.	N.R.
H_2, Ni, Pt, 120°	N.R.	$CH_3CH_2CH_3$	addition
H_2, Ni, Pt, 200°	N.R.	$CH_3CH_2CH_3$	addition
H_2, Ni, Pt	N.R.	N.R.	N.R.

SIP No. 14
Tape 1 - Work Sheet

Example No. 12 - Heats of Combustion

Cycloalkane	Heat of combustion (kcal/mole)	Heat of combustion per CH_2 group (kcal/mole)	Total Strain* (kcal/mole)	Stability
cyclopropane	499.83	166.6	27.6	min.
cyclobutane	655.86	164.0	26.4	
cyclopentane	793.52	158.7	6.5	
open chain compound	------	157.4	0	max.

*Calculated by substracting (nx157.4) from the observed heat of combustion.

n= No. of CH_2 groups

157.4 kcal/mole = heat of combustion per CH_2 group for an open chain compound

Example No. 13

Cycloalkane	Bond angles (degree)	Deviation from the tetrahedral angle (degree)	Total Strain (kcal/mole)	Stability
cyclopropane	60	49.5	27.6	min.
cyclobutane	90	19.5	26.5	
cyclopentane	108	1.5	6.5	max.

deviation from the tetrahedral angle $\propto$ angle strain $\propto$ $\frac{1}{\text{stability}}$

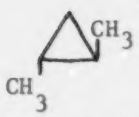
SIP No. 14
Tape 1 - Work Sheet

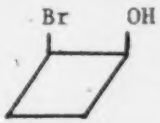
Assignment No. 10

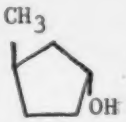
Draw the structures of all the theoretically possible stereoisomers of a) 2-bromo---cyclopentanol and b) 1,3-dibromocyclopentane. Identify the enantiomeric pairs and indicate for each stereosisomer whether it is optically active or inactive.

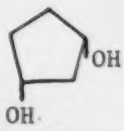
Assignment No. 11

Identify each species below as cis, trans or meso and for each state whether it would be optically active or inactive when separated.

a) 

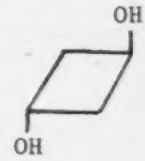
b) 

c) 

d) 

e)

f)

g) 

SIP No. 14
Tape 1 - Work Sheet

Example No. 14

Planar Conformations

cyclopropane cyclobutane cyclopentane

Nonplanar Conformations

"Butterfly" conformation "Twist" conformation "Envelope" conformation

Assignment No. 9 - Structural isomerism of the alicylic compounds

Draw the structures and name all the possible structural isomers of:

a) dimethyl cyclobutane

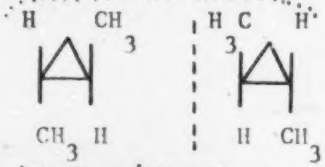
b) dimethyl cyclopentane

c) dimethyl cyclohexane

Example No. 15 - Stereoisomerism of 1,2-dimethyl cyclopropane

Cis-isomer
optically inactive

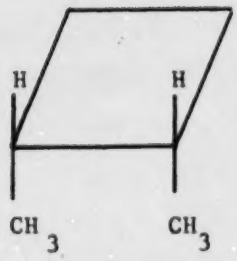
enantiomeric pair



trans - isomers
optically active
(nonsuperimposable)

SIP No. 14
Tape I - Work Sheet

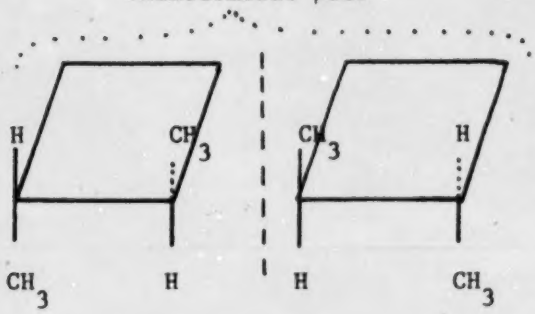
Example No. 16 - Stereoisomerism of 1,2-dimethyl cyclobutane



cis isomer

optically inactive

enantiomeric pair



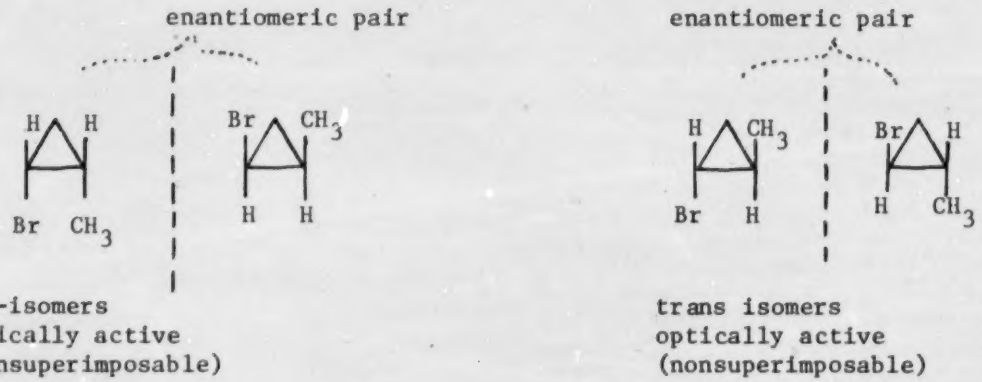
trans isomers

optically active

(nonsuperimposable)

SIP No. 14
Tape 1 - Work Sheet

Example No. 17 - Stereoisomerism of 1-bromo-2-methyl cyclopropane



Assignment No. 12

Outline all steps in a possible laboratory synthesis of the following products from 2- entanol.

a) racemic trans-1-methyl-2-ethyl-3,3-dichlorocyclopropane

b) 1,2-diethyl cyclopropane

Assignment No. 13

Describe simple chemical tests that would distinguish between:

a) cyclobutane and 2-butene

SIP No. 14
Tape 1 - Work Sheet

Assignment No. 13 (continued)

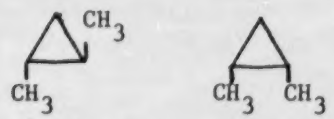
b) cyclopropane and propane

c) cyclobutane and 1-butyne

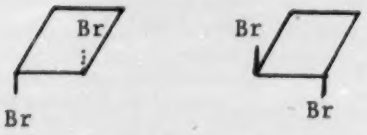
d) cyclopropane and cyclobutane

Assignment No. 14

Identify each pair of compounds as: diastereoisomers, enantiomers, structural isomers, same or different.

a) 

_____

b) 

_____

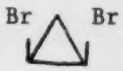
c)

_____

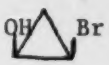
SIP No. 14
Tape 1 - Work Sheet

Assignment No. 14

d)



e)



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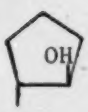
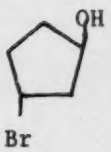




Assignment No. 15

You have two bottles having the same label - 1,2-dibromocyclopentane. However these two compounds have different boiling points - one has a boiling point of 138.5 °C and the other has a boiling point of 141 °C. How could you decide beyond any doubt which one should be labeled "cis" and which "trans"?

If a little knowledge is dangerous, where is the man who has so much as to be out of danger? T.H. Huxley (1877)

Self Instructional Package No. 14
Tape 2 - Work Sheet

ALICYCLIC COMPOUNDS

CYCLOHEXANE

Example No. 1

Cycloalkane $(CH_2)_n$		Deviation from the Tetrahedral angle (degree)	Heat of combustion per CH_2 group (kcol/mole)	Angle Strain (kcol/mole)
n=3		49.5	166.6	27.6
n=4		19.5	164.	26.4
n=5		1.5	158.7	6.5
n=6		(10.5)* 0	157.4	0
n=7		(19.0)*	158.3	6.3
n=8		(25.5)*	158.6	9.6

*deviation from the tetrahedral angle calculated for planar ring as per Baeyer theory

SIP No. 14
Tape 2 - Work Sheet

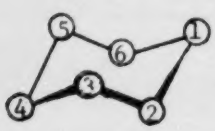
Example No. 2 - Conformations of cyclohexane

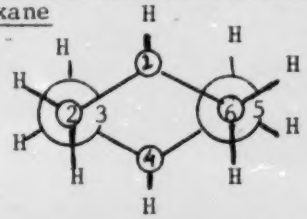
Chair form

Boat form

Twist form

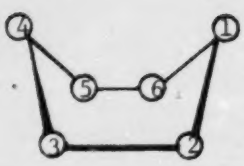
Example No. 3 - Staggered and eclipsed bonds in different conformations of cyclohexane

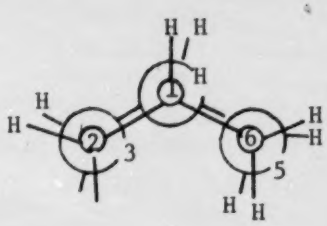




(staggered)

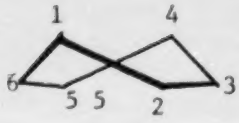
CHAIR CONFORMATION

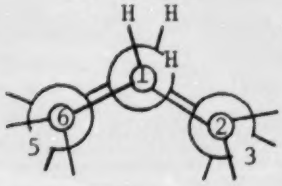




(eclipsed)

BOAT CONFORMATION

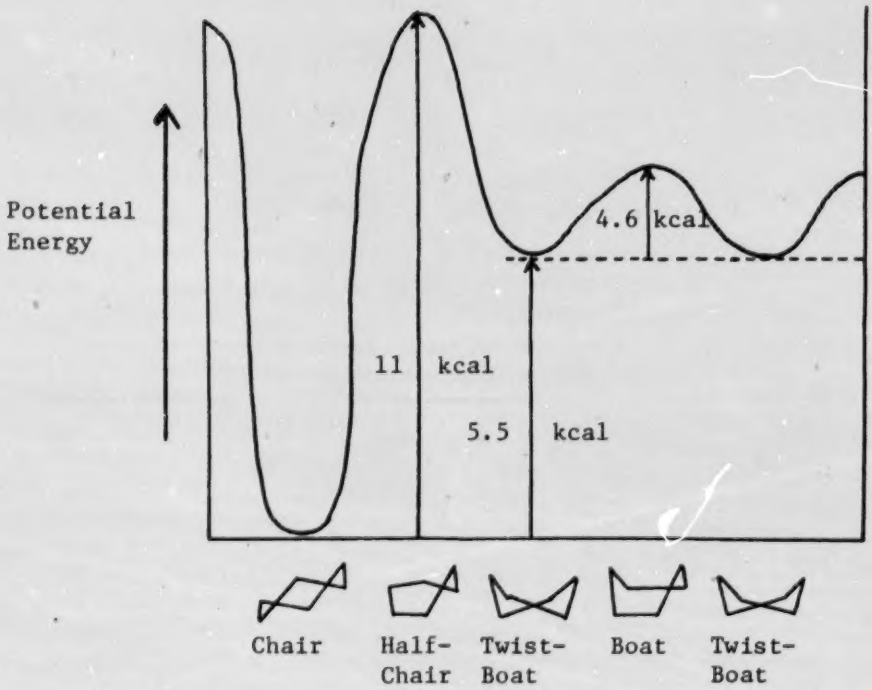




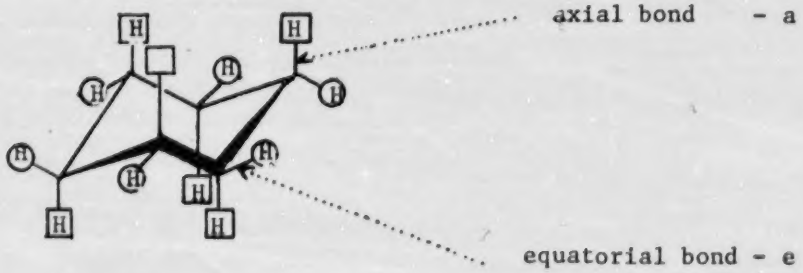
TWIST CONFORMATION

SIP No. 14
Tape 2 - Work Sheet

Example No. 4 - Potential energy relationship between different conformations of cyclohexane

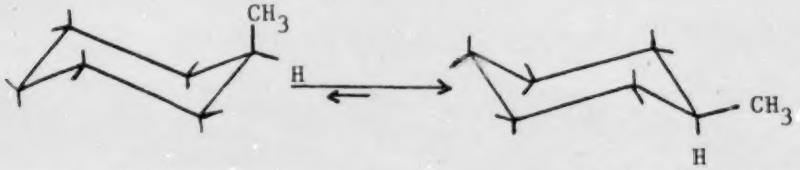


Example No. 5 - Equatorial and axial bonds in chair cyclohexane



SIP No. 14
Tape 2 - Work Sheet

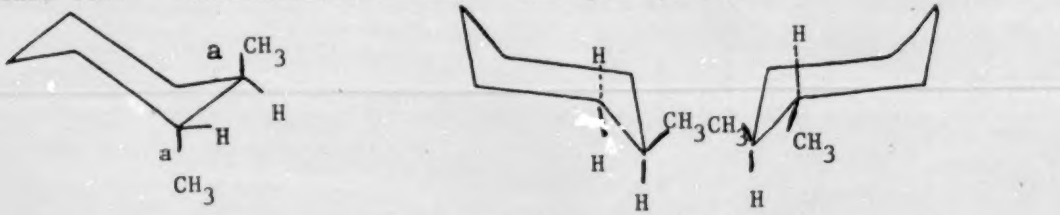
Example No. 6 - Conformational isomers of methylcyclohexane



a - methyl cyclohexane e - methyl cyclohexane , (more stable)

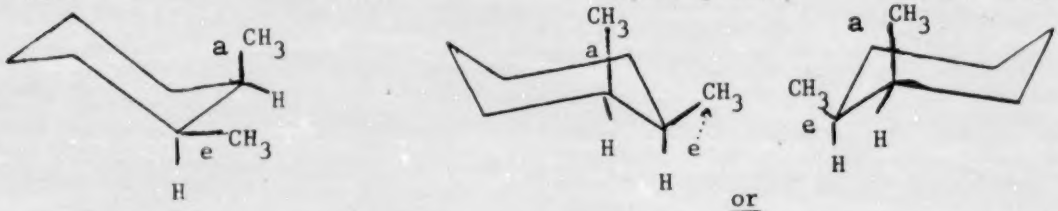
Example No. 7 - Stereoisomerism of 1,2-dimethyl cyclohexane

Trans form conformational isomers Nonsuperimposable mirror images

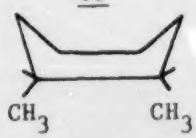


diequatorial conformers of trans isomer

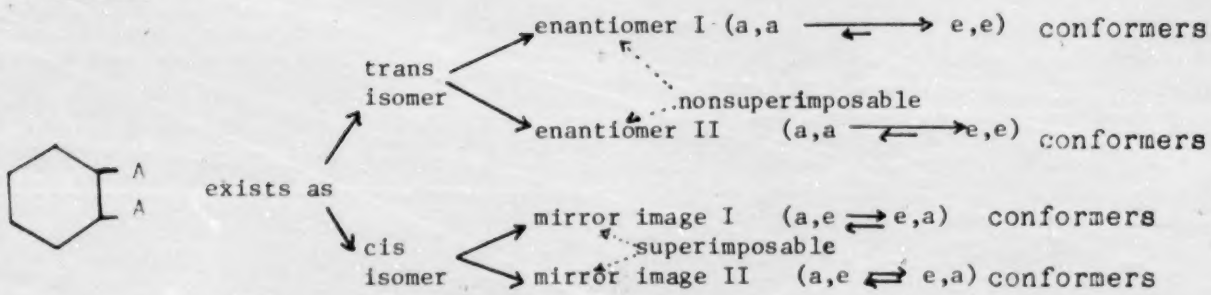
Cis form conformational isomers Superimposable mirror images



(a) or

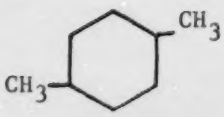


Summary:

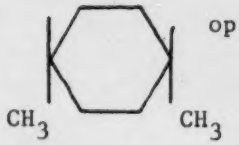


SIP No. 14
Tape 2 - Work Sheet

Example No. 8 - Stereoisomerism of 1,4-dimethyl cyclohexane



exists in two diastereoisomeric forms



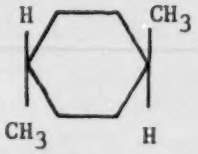
optically inactive isomer

a meso form

possesses a plane of symmetry

cis isomer

(a,e $\rightleftharpoons$ e, a conformers)



optically inactive isomer

a meso form

possesses a plane of symmetry

trans isomer

(a,a $\rightleftharpoons$ e,e conformers)

Assignment No. 1

Draw all the possible stereoisomers, identify cis and trans isomers, configurational and conformational isomers, optically active and inactive isomers of 1,3-dimethyl cyclohexane.

SIP No. 14
Tape 2 - Work Sheet

Assignment No. 2

Compare stabilities and draw structures of the possible chair conformations of: a) cis-1,2-dimethylhexane, b) cis-2-methyl cyclohexanol, c) trans-4-bromo cyclohexanol and d) trans-1,4-dimethyl cyclohexane.

Assignment No. 3

On the basis of 0.9 kcal/mole per 1,3-diaxial methyl-hydrogen interaction and 3.6 kcal/mole per 1,3-diaxial methyl-methl interaction, predict the potential energy difference between the conformational isomers of cis-1,3-dimethyl cyclohexane.

Assignment No. 4

The reactions below are carried out and thep oducts are separated by different laboratory techniques (distillation, crystalization or chromatography). Identify the fractions that will be obtained in each reaction. Tell whether each fraction collected will be optically active or inactive.

a) R -3-hydroxycyclohexene + $KMnO_4$ ⟶

b) S - chlorocyclopentane + Cl_2 $\xrightarrow{\text{heat}}$

SIP No. 14
Tape 2 - Work Sheet

Assignment No. 4 (continued)

c) racemic 3-hydroxy cyclopentene + H_2O $\xrightarrow{\text{acid}}$

Assignment No. 5

The magnitude of the equilibrium constant for the char - boat interconversion of substituted cyclohexanes is dependent on the substituent. The equilibrium constant for the interconversion of a-methyl cyclohexane $\rightleftharpoons$ e-methylcyclohexane is about 20; that for a-t-butyl-cyclohexane $\rightleftharpoons$ e-t-butylcyclohexane is 1000 or greater. Explain this considerable difference in the equilibrium constant.

Assignment No. 6

Which of the compounds below are resolvable and which are non-resolvable? Which are truly meso compounds?

	resolvable	non-resolvable	meso
a) cis-1,2-cyclohexanediol			
b) trans-1,2-cyclohexanediol			
c) cis-1,3-cyclohexanediol			
d) trans-1,3-cyclohexanediol			
e) cis-1,4-cyclohexanediol			
f) trans-1,4-cyclohexanediol			

Self Instructional Package No. 14
Tape 1 - Answer Sheet

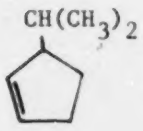
ALICYCLIC COMPOUNDS

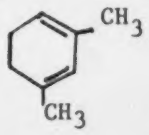
SMALL RING COMPOUNDS

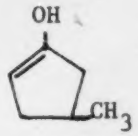
Assignment No. 1

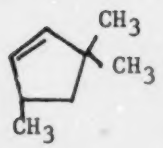
a) 1-methyl-1,3-cyclohexadiene
b) 3-ethyl cyclopentanol
c) 1,3,5-cycloheptatriene
d) cyclopentyne

Assignment No. 2

a) 







Assignment No. 3

a) 4-isopropyl cyclohexene
b) 5-methyl-1,3-cyclopentadiene
c) methylcyclopropane (correct)
d) 3-ethyl cyclohexene

Assignment No. 4

bromocycloheptane $\xrightarrow{\text{KOH alc}}$ cycloheptene

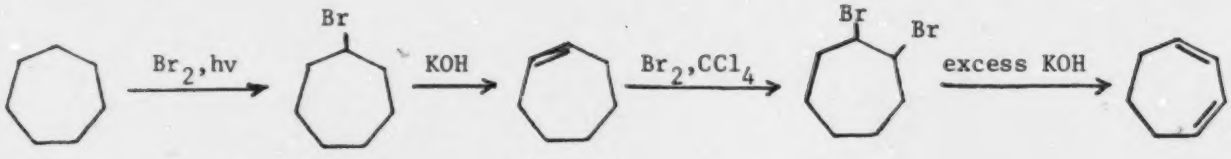
1,2-dibromocyclopentane $\xrightarrow{\text{Zn}}$ cyclopentene

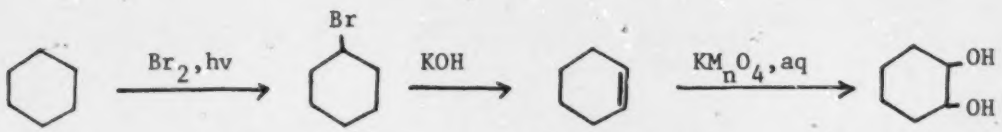
1,2-dibromocyclohexane $\xrightarrow{\text{KOH}}$ $\xrightarrow{NaNH_2}$ cyclohexyne

cyclopropene $\xrightarrow{H_2,Pt}$ cyclopropane

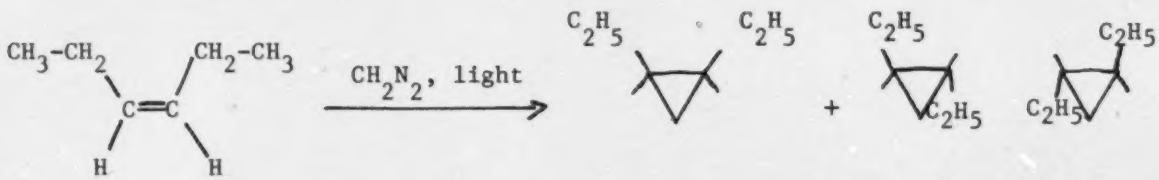
SIP No. 14
Tape 1 - Answer Sheet

Assignment No. 5

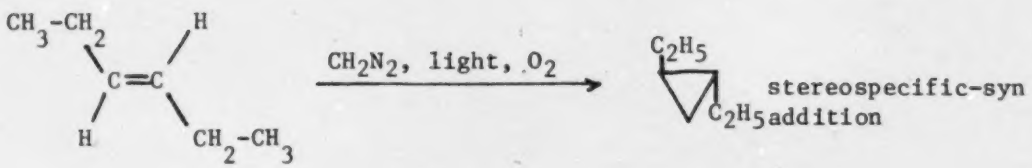




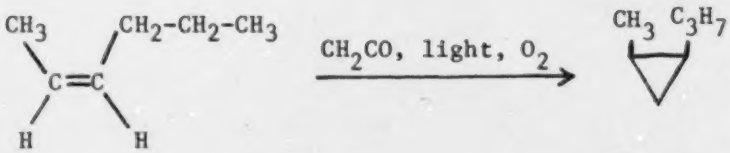
Assignment No. 6



nonstereospecific addition



stereospecific-syn addition



stereospecific-syn addition

(O_2 acts as inhibitor and inhibits the existence of triplet methylene a diradical)

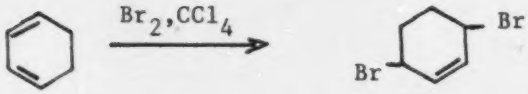
SIP No. 14
Tape 1 - Answer Sheet

Assignment No. 7

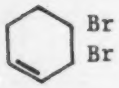
a)

bromocyclopentane

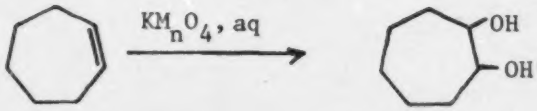
cyclopentene

b) 

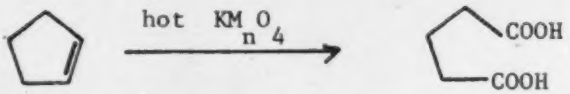
3,6-dibromocyclohexane

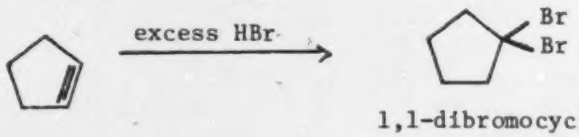


3,4-dibromocyclohexane

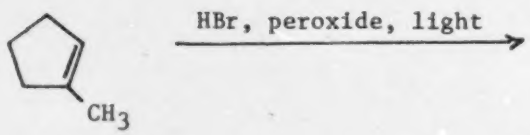
c) 

1,2-cycloheptanediol

d) 

e) 

1,1-dibromocyclopentane

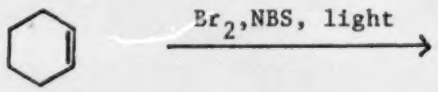
f) 

1-bromo-2-methylcyclopentane

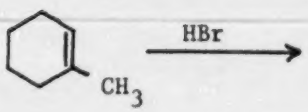
40

SIP No. 14
Tape 1 - Answer Sheet

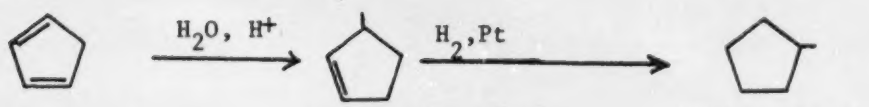
Assignment No. 7 (continued)

g) 

3-bromocyclohexene

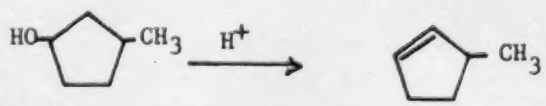
h) 

1-bromo-1-methylcyclohexane

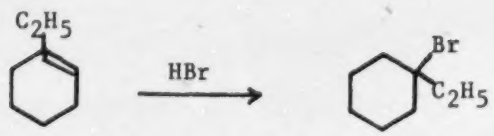
i) 

cyclopentene-3-ol cyclopentanol

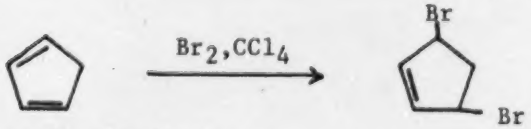
Assignment No. 8

a) 

3-methylcyclohexanol

b) 

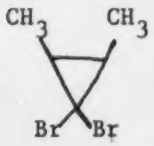
1-ethyl cyclohexene

c) 

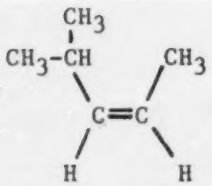
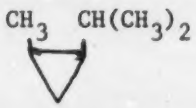
1,3-cyclopentadiene

SIP No. 14
Tape 1 - Answer Sheet

Assignment No. 8 (continued)

d) $CH_3-CH=CH-CH_3$ $\xrightarrow{CHBr_3,\ tBuO^-K^+}$ 

2-butene

e)  $\xrightarrow{CH_2N_2,\ O_2,\ light}$ 

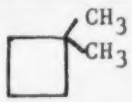
cis-4-methyl-2-pentene

f) $\xrightarrow{excess\ HBr}$

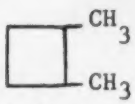
cyclobutyne

g) $\xrightarrow{O_3,H_2O,Zn}$ $OHC-CH_2-CH_2-CH_2-CHO$

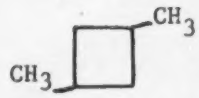
Assignment No. 9



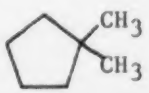
1,1-dimethylcyclobutane



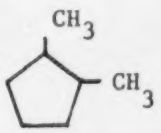
1,2-dimethyl cyclobutane



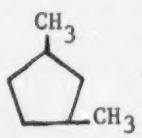
1,3-dimethylcyclobutane



1,1-dimethylcyclopentane



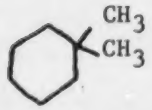
1,2-dimethylcyclopentane



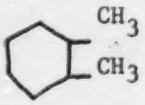
1,3-dimethylcyclopentane

SIP No. 14
Tape 1 - Answer Sheet

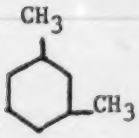
Assignment No. 9 (continued)



1,1-dimethyl cyclohexane



1,2-dimethyl cyclohexane



1,3-dimethyl cyclohexane

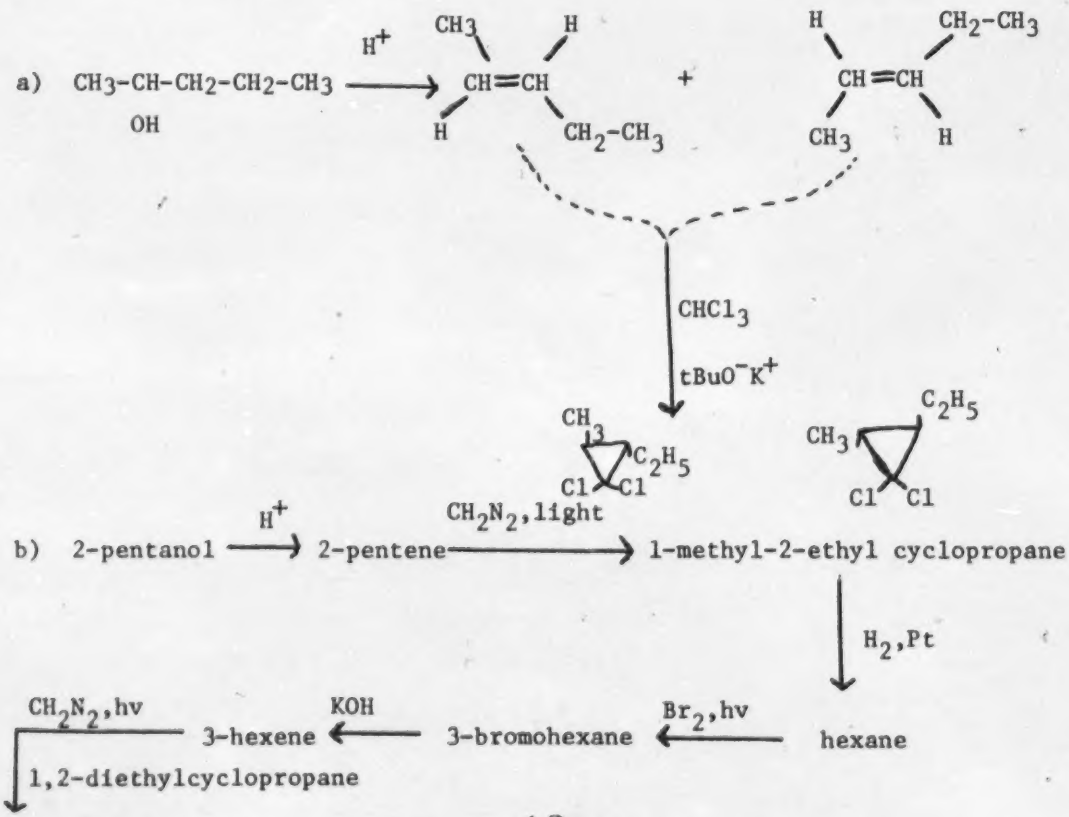
1,4-dimethyl cyclohexane

**The answer to Assignment No. 10 is on the last page.*

Assignment No. 11

a) trans, optically active
b) cis, optically active
c) trans, optically active
d) cis, meso, optically inactive
e) cis, meso, optically inactive
f) trans, optically active
g) trans

Assignment No. 12



SIP No. 14
Tape 1 - Answer Sheet

Assignment No. 13

a) $\xrightarrow{KMnO_4,\ aq}$ N.R.

$CH_3-CH=CH-CH_3 \xrightarrow[\text{purple}]{KMnO_4,aq} CH_3-\underset{OH}{CH}-\underset{OH}{CH}-CH_3 + MnO_2\downarrow$ brown precipitate

b) $\xrightarrow[\text{brown}]{Br_2,FeBr_3} BrCH_2-CH_2-CH_2Br$ colorless

$CH_3\ CH_2\ CH_3 \xrightarrow{Br_2,FeBr_3}$ N.R.

c) $\xrightarrow{Ag(NH_3)_2Cl}$ N.R.

$HC\equiv C-CH_2-CH_3 \xrightarrow{Ag(NH_3)_2Cl} Ag^{+-}\ C\equiv C-CH_2-CH_3\downarrow$ white precipitate

d) $\xrightarrow[\text{purple}]{KMnO_4}$ $\underset{OH}{CH_2}-\underset{OH}{CH_2}-CH_2 + MnO_2\downarrow$

$\xrightarrow{KMnO_4}$ N.R.

SIP No. 14
Tape 1 - Answer Sheet

Assignment No. 14

a) diastereoisomers

b) enantiomers

c) different, none of the above

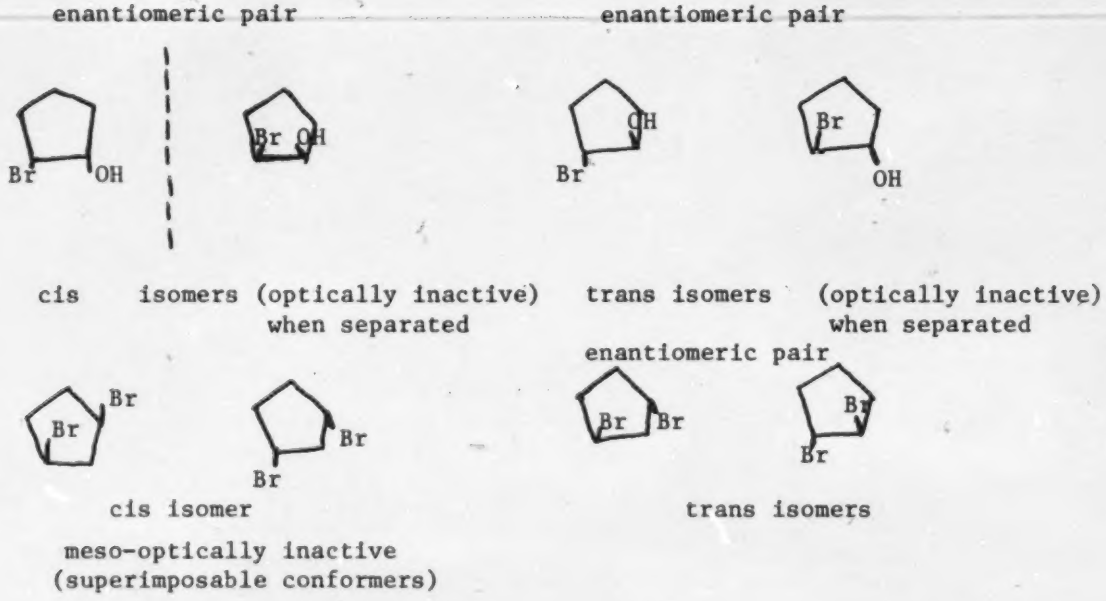
d) same (meso compound)

e) enantiomers

Assignment No. 15

Trans 1,2-dibromocyclopentane can be resolved

Assignment No. 10

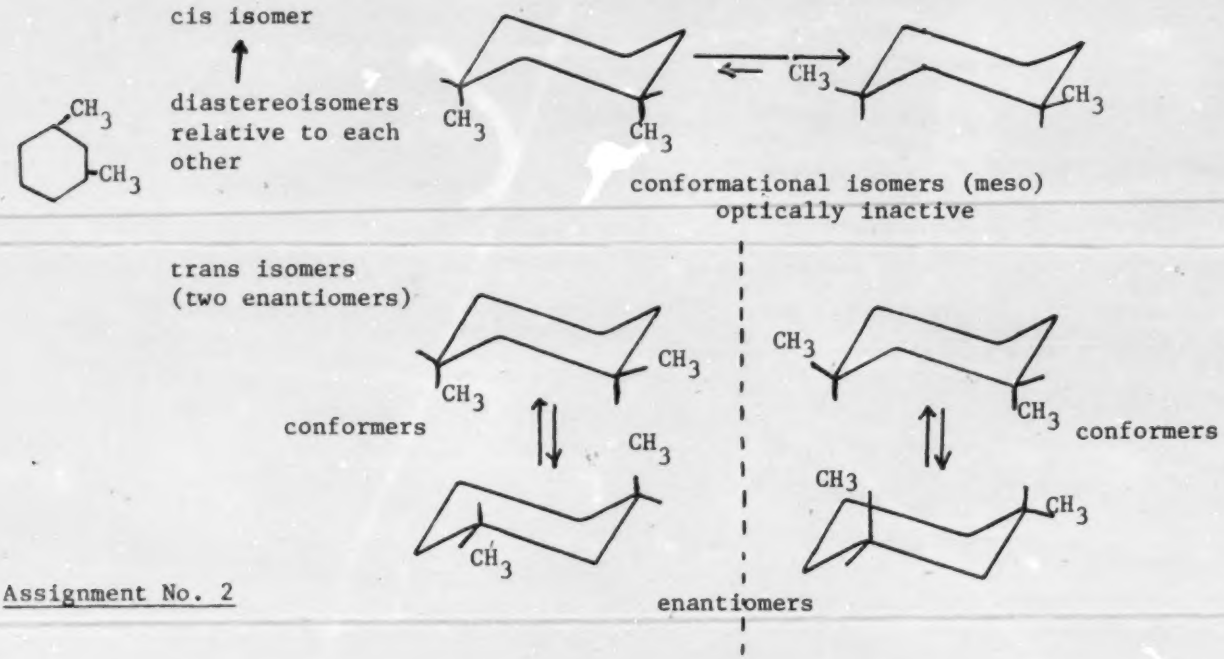


Self Instructional Package No. 14
Tape 2 - Answer Sheet

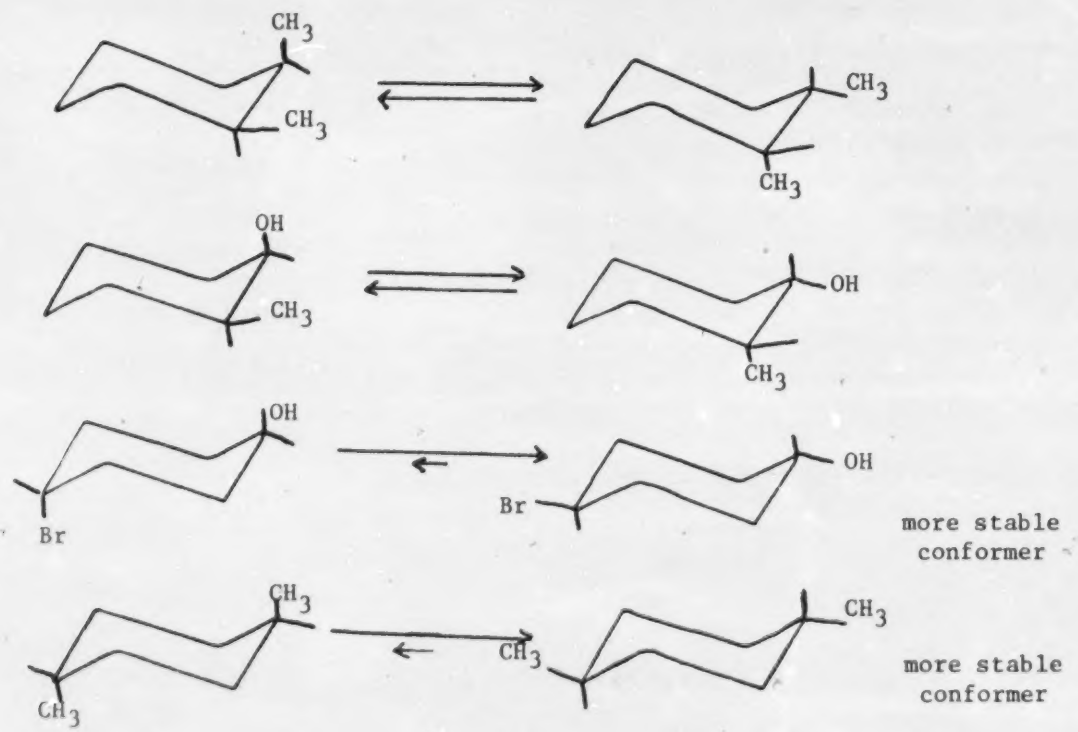
ALICYCLIC COMPOUNDS

CYCLOHEXANE

Assignment No. 1 - Stereoisomeric forms of 1,3-dimethyl cyclohexane



Assignment No. 2



SIP No. 14
Tape 2 - Answer Sheet

Assignment No. 3

cis 1,3-dimethyl cyclohexane exists in two conformational forms: I. diaxial 1,3-dimethyl cyclohexane, and II. diequatorial dimethyl-cyclohexane.

In I:

There are two 1,3-diaxial methyl-hydrogen interaction = 1.8 kcal/mole
There is one 1,3-diaxial methyl-methyl interaction = 3.6 kcal/mole

Total- 5.4 kcal/mole

In II:

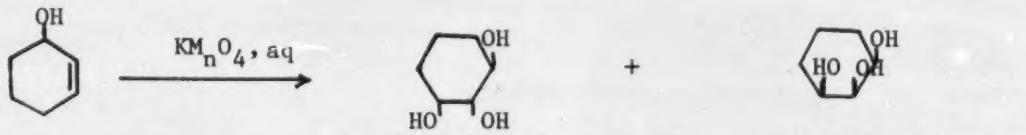
There are no 1,3-diaxial interactions

$E_I > E_{II}$ by approximately 5.4 kcal/mole

Stability I < Stability II by approximately 5.4 kcal/mole

Assignment No. 4

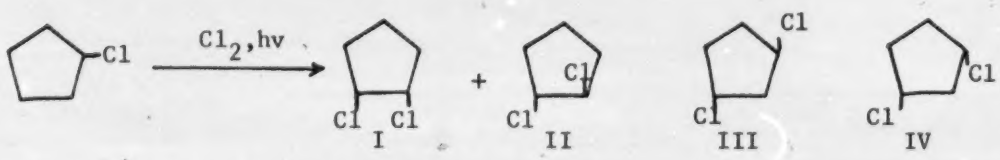
a)



optically active optically inactive

two fractions; two diastereoisomers

b)

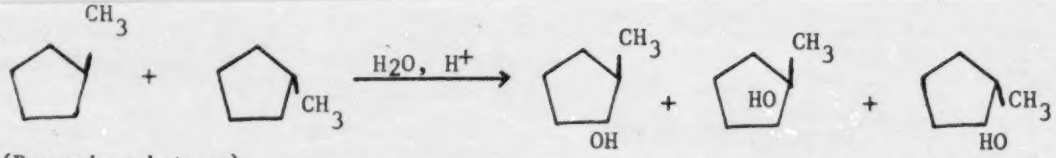


Four fractions - each is optically active when separated.

I and II are diastereoisomers
III and IV are diastereoisomers

SIP No. 14
Tape 2 - Answer Sheet

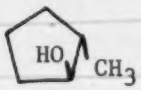
Assignment No. 4 (continued)

c) 

(Racemic mixture) I II III

Two fractions - optically inactive

I and IV are enantiomers - racemic mixture
II and III are enantiomers - racemic mixture



IV

Assignment No. 5

Energy difference caused by the 1,3-diaxial alkyl-hydrogen interaction increases with the size of the alkyl group. Steric hindrance becomes a prominent factor with the increase in the size of the alkyl group.

Assignment No. 6

	resolvable	non-resolvable	meso
a) cis-1,2-cyclohexanediol		X	X
b) trans-1,2-cyclohexanediol	X		
c) cis-1,3-cyclohexanediol		X	X
d) trans-1,3-cyclohexanediol	X		
e) cis-1,4-cyclohexanediol		X	
f) trans-1,4-cyclohexanediol		X	

e.f contain no chiral carbons

Self Instructional Package No. 14
Form D - Progress Check Evaluation

ALICYCLIC COMPOUNDS

Identify the statements below as True or False by placing a capital T or F in the spaces provided on the left.

1. _____ Equatorial conformation of methylcyclohexane is more stable than the axial conformation.

2. _____ Reaction of an alkene with haloform in presence of potassium tertiary butoxide is stereospecific.

3. _____ Reaction of 2-butene with diazomethane in presence of light is stereospecific.

4. _____ Reaction of cyclopentene with aqueous solution of potassium permanganate is stereospecific.

5. _____ Deviation from the tetrahedral angle in a saturated molecule generates angle strain.

6. _____ Greater the deviation from the tetrahedral angle greater the stability of the compound.

7. _____ Cycloaddition reactions of cyclopropane substantiate the validity of Baeyer theory.

8. _____ The Baeyer theory with regard to cyclohexane proved to be incorrect.

9. _____ Baeyer's misconception was that all cyclic compounds are planar.

10. _____ The twist conformer of cyclohexane is more stable than the chair conformer.

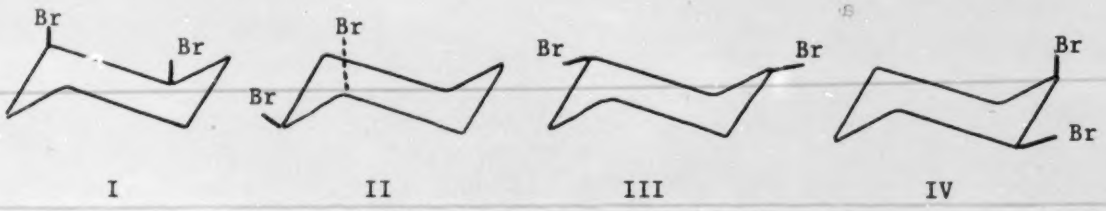
11. _____ The major product in the reaction of cyclopropane with bromine in presence of heat is bromocyclopropane.

12. _____ The major product in the reaction of cyclopropane with bromine in presence of iron is 1,3-dibromopropane.

SIP No. 14
Form D - Progress Check Evaluation

Blacken out the correct answer or answers below:

13. The correct statements with regard to the four compounds given below are:



a) II and IV cannot be separated.
b) I and III are conformational isomers.
c) I and II are structural isomers.
d) I, II, III and IV are cis isomers.

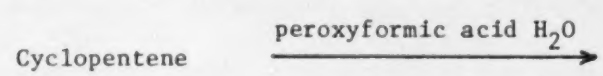
14. The correct statements about singlet methylene are:

a) It has two nonbonding electrons paired in one atomic orbital
b) It is the more stable form of methylene.
c) It adds stereospecifically to an alkene.
d) It adds to propene to yield cyclopropane.

15. The major product in the reaction below is:

a) axial, equatorial-1,2-cyclohexanediol
b) $HOOC-CH_2-CH_2-CH_2-CH_2-COOH$
c) cis 1,2-cyclohexanediol
d) trans 1,2-cyclohexanediol

16. The major product in the reaction below is:



a) cis-1,2-cyclopentanediol
b) racemic mixture of the enantiomeric trans 1,2-cyclopentanediols
c) cyclopentanol
d) $HOOC-CH_2-CH_2-CH_2-COOH$

SIP No. 14
Form D - Progress Check Evaluation

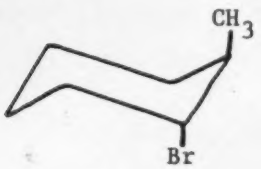
17. Relative to each other compounds

and

are:

a) enantiomers
b) diastereoisomers
c) conformational isomers
d) configurational isomers

18. The correct statements about the compounds below are:

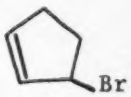


I

II

a) Relative to each other I and II are diastereoisomers
b) Relative to each other I and II are enantiomers
c) I is the conformational isomer of II
d) I is trans and II is cis isomer

19. The correct IUPAC for the compound below is:



a) 4-bromo cyclopentene
b) 1-bromo-2-cyclopentene
c) 3-bromocyclopentene
d) 3-bromo-1-cyclopentene

20. The correct statements about 1,2-cyclohexanediol are:

a) There are two diastereoisomers of 1,2-cyclohexanediol cis and trans
b) trans 1,2-cyclohexanediol exists in two conformational forms
c) There are two enantiomeric forms of 1,2-cyclohexanediol
d) cis 1,2-cyclohexanediol is optically active.

21. The correct statements about the compounds below are:

I

II

a) I and II are enantiomers relative to each other
b) Both I and II are optically active when separated
c) I and II are structural isomers relative to each other
d) Both I and II are "cis" forms

22. The reaction of cis 2-pentene with bromoform in presence of potassium tertiary butoxide yields:

a) cis 1-methyl-2-ethyl cyclopropane
b) trans 1-methyl-2-ethyl cyclopropane
c) cis 1,1-dibromo-2-methyl-3-ethyl cyclopropane
d) trans 1,1-dibromo-2-methyl-3-ethyl cyclopropane

Self Instructional Package No. 14
Form B^1 - Self Evalatuion Exercise - Answers

ALICYCLIC COMPOUNDS

1.	F	14.	a,b
2.	T	15.	b
3.	T	16.	a
4.	T	17.	a
5.	F	18.	a. c, d
6.	T	19.	a, d
7.	F	20.	b
8.	F	21.	c
9.	T	22.	d
10.	F	23.	a
11.	T	24.	b
12.	F	25.	a
13.	T		

Self Instructional Package No. 14
Form D1 - Progress Check Evaluation - Answers

ALICYCLIC COMPOUNDS

1. T
2. T
3. F
4. T
5. T
6. F
7. T
8. T
9. T
10. F
11. T
12. T
13. a, b. c, d
14. a, c
15. a, c
16. b
17. a, d
18. c
19. c
20. a, b, c
21. b, c, d
22. c